JC17 Rec'd PCT/PTO 25 JUN 2001

Form PTO-1390 (Rev. 12-29-99) US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

ATTORNEY'S DOCKET NO: H 3294 PCT/US

U S APPLICATION NO (If known, see 37 CFR 1.5): 09/869171

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/EP99/09901	December 14, 1999	December 23, 1998

TITLE OF INVENTION
AGENT FOR COLORING KERATINACEOUS FIBERS

APPLICANT(S) FOR DO/EO/US
Horst Hoeffkes, Doris Oberkobusch, David Rose, Melanie Hitz

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ■ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ■ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ■ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ■ A translation of the International Application into English (35 U.S.C 371(c)(2)).
7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau)
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ■ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S C. 371(c)(3)).
9. ■ An oath or declaration of the inventor(s) (35 U S.C. 371(c)(4)). UNEXECUTED
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern other document(s) or information included:

11. ■ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ■ A FIRST preliminary amendment
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ■ Other items or information:

    PTO Form 1449 (with references)

"Express Mail" mailing label number EL615775777US

U.S. Application No. (If known, see 37 CFR 1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
09/869171	PCT/EP99/09901	H 3294 PCT/US

17. ■ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO.....**$1000.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO.....**$860.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37CFR 1.445(a)(2)) paid to USPTO **$710.00**

International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) **$690.00**

International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4).....**$100.00**

	CALCULATIONS	PTO USE ONLY
ENTER APPROPRIATE BASIC FEE AMOUNT =	$ 860	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).	$ 0	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	1 - 20 =	0	0 X $18.00	$ 0	
Independent Claims	1 - 3 =	0	0 X $80.00	$ 0	
Multiple dependent claims (s)(if applicable)		0	+ $270.00	$ 0	
TOTAL OF ABOVE CALCULATIONS =				$ 860	
Reduction of ½ for filing by small entity, if applicable. A Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				$ 0	
SUBTOTAL =				$ 860	
Processing fee of **$130.00** for furnishing the English translation later the ☐ 20 ☐ 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +				$ 0	
TOTAL NATIONAL FEE =				$ 860	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40.00 per property +				$ 0	
TOTAL FEES ENCLOSED =				$ 860	
				Amount to be: refunded:	$----------
				charged:	$ 860. 00

a. ☐ A check in the amount of $_____ to cover the above fees is enclosed.

b. ■ Please charge my Deposit Account No. 01-1250 in the amount of $ 860.00 to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. 01-0498.

c. ■ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 01-1250. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Henkel Corporation, Law Dept.
2500 Renaissance Blvd., Suite 200
Gulph Mills, PA 19406

Kimberly R. Hild
SIGNATURE:

Kimberly R. Hild
NAME ATTORNEY FOR APPLICANT

39,224
REGISTRATION NUMBER

PATENT
Docket No. H 3294 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Hoeffkes, et al.

International Application No. PCT/EP99/09901
International Filing Date: December 14, 1999

Serial No. To be assigned
Filed: To be assigned

Examiner: To be assigned
Art Unit: To be assigned

Title: AGENT FOR COLORING KERATINACEOUS FIBERS

"Express Mail Post Office to Addressee" service mailing label number EL615775777US

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification (Using the English Translation):

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following header and paragraph on consecutive lines as shown below:

-- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP99/09901 filed on December 14, 1999, the international

application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 198 59 800.9, filed on December 23, 1998. --

On page 1, on a separate line immediately after the above inserted paragraph and before line 1, please insert the following header:
-- FIELD OF THE INVENTION --.

On page 1, on a separate line between lines 6 and 7, please insert the following header:
-- BACKGROUND OF THE INVENTION -- .

On page 3, on a separate line between lines 16 and 17, please insert the following header:
-- SUMMARY OF THE INVENTION --.

On page 7, on a separate line between lines 19 and 20, please insert the following header:
-- DETAILED DESCRIPTION OF THE INVENTION --.

On page 26, line 1, please replace the heading "Patent claims" with the following heading:
-- What is claimed is: --

On a separate page, after page 40, please insert the enclosed Abstract of the Disclosure.

In the Claims

Please cancel Claims 2 to 13, without prejudice.

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claim 1 will be pending after entry of the present amendment. Claims 2 to 13 are being canceled without prejudice.

Amendment

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance with 37 CFR §1.78 and to claim priority to those applications listed therein.

Applicants submit herewith "Version With Markings To Show Changes Made" to show the amendments made to the specification.

CONCLUSION

The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

Kimberly R. Hild

Kimberly R. Hild
(Reg. No. 39,224)
Attorney for Applicants
(610) 278-4964

Henkel Corporation
Law Department
2500 Renaissance Boulevard, Suite 200
Gulph Mills, PA 19406

Abstract of the Disclosure

The present invention relates to a composition for coloring keratinaceous fibers and a method of using the same. The composition of the present invention contains (a) at least one pyrimidine derivative and (b) at least one compound selected from an m-phenylene derivative, an m-aminophenol derivative, a pyridine derivative, a resorcinol derivative, a methylenedioxybenzene derivative, or 3,4-diaminobenzoic acid or combinations thereof. The method of the present invention includes applying the coloring composition to keratin-containing fibers and subsequently rinsing the coloring composition from the fibers.

PATENT
Docket No. H 3294 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Hoeffkes, et al.

International Application No. PCT/EP99/09901
International Filing Date: December 14, 1999

Serial No. 09/869,171 **Examiner:** To be assigned
Filed: To be assigned **Art Unit:** To be assigned

Title: AGENT FOR COLORING KERATINACEOUS FIBERS

"Express Mail Post Office to Addressee" service mailing label number EL615775485US

SUPPLEMENTAL PRELIMINARY AMENDMENT

Box PCT Attn: DO/EO/US
Assistant Commissioner for Patents
Washington, DC 20231

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification

Please replace the paragraph on page 23, lines 2 to 4 with the following new paragraph:

-- Hair dyeing agents according to the invention were in the form of a hair dyeing cream emulsion of the composition given in Table 1. --

In the Claims

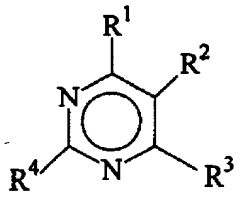
Please cancel Claim 1, without prejudice.

Please add the following new claims:

14. (NEW) A method of coloring keratin fibers comprising

(A) applying to keratin fibers a coloring composition formed from components comprising

(a) at least one pyrimidine derivative of formula I

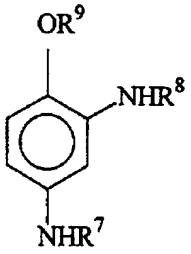


(I)

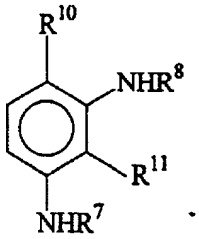
wherein R^1, R^2, R^3 and R^4 are, independently of one another, selected from hydrogen, an OH group, a NH_2 group, or a NR^5R^6 group, wherein R^5 and R^6 are independently selected from a C_1 to C_4 alkyl group, or a C_1 to C_4 hydroxyalkyl group having one or more hydroxyl groups that are primary, secondary or combinations thereof, or where two of the R^1, R^2, R^3 or R^4 substituents together form a 5 or 6 member, optionally substituted, heterocycle ring containing one or two nitrogen atoms, or one or two oxygen atoms or a combination of both in the heterocycle ring, with the proviso that at least two of the R^1, R^2, R^3 or R^4 substituents are a NH_2 group or NR^5R^6 group, and

(b) at least one compound selected from

(i) m-phenylene derivatives of formula II or III

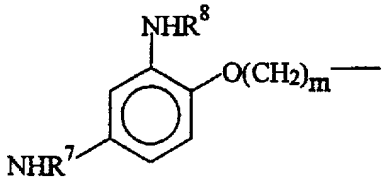


(II)



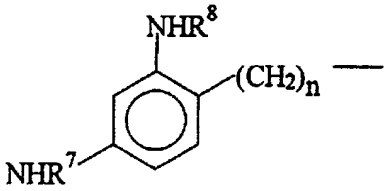
(III)

wherein R^7, R^8 and R^{11} are independently from one another hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, R^9 is a C_1 to C_4 hydroxyalkyl group or a radical of formula IV



(IV)

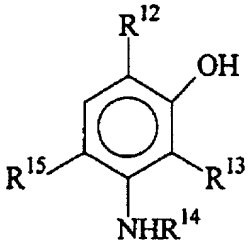
in which R^7 and R^8 are defined as above and m is an integer from 1 to 4, and R^{10} is hydrogen or a radical of formula V



(V)

in which R^7 and R^8 are as defined above and n is an integer from 1 to 4,

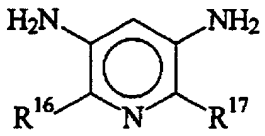
(ii) m-aminophenol derivatives of formula (VI)



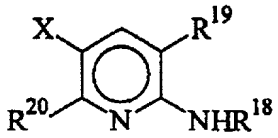
(VI)

wherein R^{12} is hydrogen or a C_1 to C_4 alkyl group, R^{13} is hydrogen, fluorine, chlorine, an OCH_3 group or a C_1 to C_4 alkyl group, R^{14} is hydrogen, a C_1 to C_4 alkyl group, a C_1 to C_4 hydroxyalkyl group or an OCF_3 group, R^{15} is hydrogen, fluorine, chlorine or an OCH_3 group, with the provisos that R^{12}, R^{13}, R^{14} and R^{15} are not hydrogen at the same time, and that, if R^{12} is methyl, R^{13}, R^{14} and R^{15} are not hydrogen at the same time,

(iii) pyridine derivatives of formula VII or VIII



(VII)

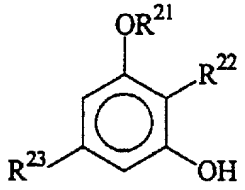


(VIII)

wherein R^{16} and R^{17} are independently fluorine, chlorine or an OCH_3 group, R^{18} is hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, R^{19} is an OH group or NH_2 group, R^{20} is hydrogen, a C_1 to C_4 alkoxy group or a NH_2 group, X is hydrogen or

an OCH_3 group, with the provisos that, if R^{19} is NH_2, R^{18} and R^{20} are not a C_1 to C_4 alkyl group and a methoxy group, respectively, at the same time, and if R^{18} is hydrogen, R^{19} and R^{20} are not an OH group and hydrogen, respectively, at the same time,

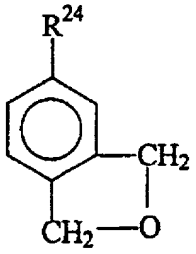
(iv) resorcinol derivatives of formula IX



(IX)

wherein R^{21}, R^{22} and R^{23} are independently from one another hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, with the provisos that R^{21}, R^{22} and R^{23} are not hydrogen at the same time, R^{22} is not methyl if R^{21} and R^{23} are hydrogen, and R^{22} and R^{23} are not hydrogen at the same time if R^{21} is methyl,

(v) methylenedioxybenzene derivatives of formula X



(X)

wherein R^{24} is an OH group, a NH_2 group or a NHR^{25} group, in which R^{25} is a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl, or

(vi) 3,4-diaminobenzoic acid, or

(vii) combinations thereof; and

(B) oxidatively developing the coloring composition using atmospheric oxygen, an enzyme containing system, or combinations thereof as the sole oxidizing agent.

15. (NEW) The method of claim 14 wherein the pyrimidine derivative is 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine, 2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, or 4-methylamino-2,5,6-tetraminopyrimidine, or combinations thereof.

16. (NEW) The method of claim 15 wherein the pyrimidine derivative is 2,4,5,6-tetra-aminopyrimidine.

17. (NEW) The method of claim 15 wherein the pyrimidine derivative is present in the coloring composition in an amount of from 0.03 mmol to 65 mmol, based on 100 g of the coloring composition as a whole.

18. (NEW) The method of claim 14 wherein at least one of R^7 and R^8 of the Formula III is a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, and wherein R^{20} of the Formula VIII is hydrogen or a C_1 to C_4 alkoxy group.

19. (NEW) The method of claim 14 wherein the component B comprises 1,3-bis(2,4-diaminophenoxypropane), 1,3-bis(2,4-diaminophenylpropane), 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, or N-(2-hydroxyethyl)-3,4-methylenedioxyaniline, or combinations thereof.

20. (NEW) The method of claim 19 wherein each compound of component B is present in the coloring composition in an amount of 0.03 mmol to 65 mmol, based on 100 g of the coloring composition as a whole.

21. (NEW) The method of claim 14 wherein the coloring composition further comprises at least one activated carbonyl compound selected from the group consisting of isatin, 5-chloroisatin, 5-bromoisatin, 6-bromoisatin, 5-nitroisatin, N-hydroxymethylisatin, N-allylisatin, 5-isatinsulfonic acid Na salt, glutaconaldehyde tetrabutylammonium salt, tribase aldehyde, malonaldehyde bis(dimethyl acetal), 4-hydroxy-3-methoxycinnanaldehyde, 1-piperidino-methylisatin, 1-diethylaminomethylisatin, glutaconaldehyde Na salt, 5-N-methylanilinopenta-dienyl, 2-chloro-3-hydroxymethylene-1-cyclohexene 1-aldehyde, N-(5-anilino-2,4-pentanedien-1-ylidene)anilinium chloride, trans-β-(2-furyl)acrolein, 2-nitro-1,3-indanedione, dehydroascorbic acid, 2-acetyl-1,3-cyclohexanedione, 7-dimethylamino-2,4,6-heptatrienylidene dimethylammonium perchlorate, 4-formyl-1-methylpyridinium benzenesulfonate, and combinations thereof.

22. (NEW) The method of claim 14 wherein the coloring composition further comprises one or more compounds selected from 5,6-dihydroxyindole or its N-substituted C_1 to C_4 alkyl or C_1 to C_4 hydroxyalkyl derivatives, or 5,6-dihydroxyindoline or its N-substituted C_1 to C_4 alkyl or C_1-C_4-hydroxyalkyl derivatives or combinations thereof.

23. (NEW) The method of claim 14 wherein the coloring composition further comprises one or more compounds selected from p-phenylenediamine, p-tolylenediamine, p-aminophenol, 4,4'-diaminodiphenylamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2,(2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 5-aminosalicylic acid, bis(2-hydroxy-5-aminophenyl)methane, or 2-(2,5-diaminophenoxy)ethanol, or combinations thereof.

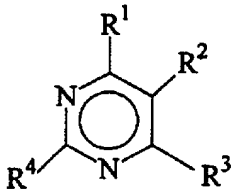
24. (NEW) The method of claim 14 wherein the coloring composition further comprises anionic surfactants, zwitterionic surfactants, nonionic surfactants, or combinations thereof.

25. (NEW) The method of claim 14 wherein the coloring composition is combined with an enzyme containing system before the application of the coloring composition to the keratin fibers.

26. (NEW) A method of coloring keratin fibers comprising

(A) applying to keratin fibers

(a) at least one pyrimidine derivative of formula I

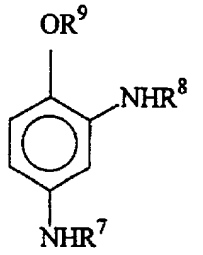


(I)

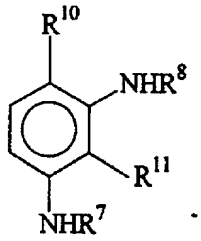
wherein R^1, R^2, R^3 and R^4 are, independently of one another, selected from hydrogen, an OH group, a NH_2 group, or a NR^5R^6 group, wherein R^5 and R^6 are independently selected from a C_1 to C_4 alkyl group, or a C_1 to C_4 hydroxyalkyl group having one or more hydroxyl groups that are primary, secondary or combinations thereof, or where two of the R^1, R^2, R^3 or R^4 substituents together form a 5 or 6 member, optionally substituted, heterocycle ring containing one or two nitrogen atoms, or one or two oxygen atoms or a combination of both in the heterocycle ring, with the proviso that at least two of the R^1, R^2, R^3 or R^4 substituents are a NH_2 group or NR^5R^6 group; and

(b) at least one compound selected from

(i) m-phenylene derivatives of formula II or III

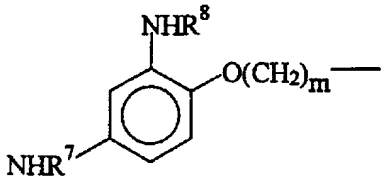


(II)



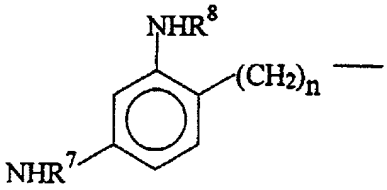
(III)

wherein R^7, R^8 and R^{11} are independently from one another hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, R^9 is a C_1 to C_4 hydroxyalkyl group or a radical of formula IV



(IV)

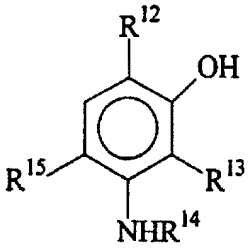
in which R^7 and R^8 are defined as above and m is an integer from 1 to 4, and R^{10} is hydrogen or a radical of formula V



(V)

in which R^7 and R^8 are as defined above and n is an integer from 1 to 4,

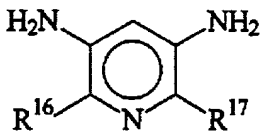
(ii) m-aminophenol derivatives of formula (VI)



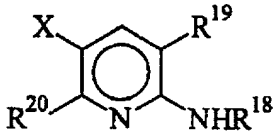
(VI)

wherein R^{12} is hydrogen or a C_1 to C_4 alkyl group, R^{13} is hydrogen, fluorine, chlorine, an OCH_3 group or a C_1 to C_4 alkyl group, R^{14} is hydrogen, a C_1 to C_4 alkyl group, a C_1 to C_4 hydroxyalkyl group or an OCF_3 group, R^{15} is hydrogen, fluorine, chlorine or an OCH_3 group, with the provisos that R^{12}, R^{13}, R^{14} and R^{15} are not hydrogen at the same time, and that, if R^{12} is methyl, R^{13}, R^{14} and R^{15} are not hydrogen at the same time,

(iii) pyridine derivatives of formula VII or VIII



(VII)

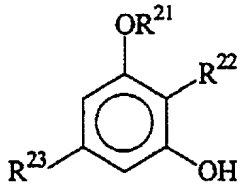


(VIII)

wherein R^{16} and R^{17} are independently fluorine, chlorine or an OCH_3 group, R^{18} is hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, R^{19} is an OH group or NH_2 group, R^{20} is hydrogen, a C_1 to C_4 alkoxy group or a NH_2 group, X is hydrogen or

an OCH_3 group, with the provisos that, if R^{19} is NH_2, R^{18} and R^{20} are not a C_1 to C_4 alkyl group and a methoxy group, respectively, at the same time, and if R^{18} is hydrogen, R^{19} and R^{20} are not an OH group and hydrogen, respectively, at the same time,

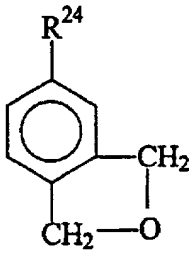
(iv) resorcinol derivatives of formula IX



(IX)

wherein R^{21}, R^{22} and R^{23} are independently from one another hydrogen, a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, with the provisos that R^{21}, R^{22} and R^{23} are not hydrogen at the same time, R^{22} is not methyl if R^{21} and R^{23} are hydrogen, and R^{22} and R^{23} are not hydrogen at the same time if R^{21} is methyl,

(v) methylenedioxybenzene derivatives of formula X



(X)

wherein R^{24} is an OH group, a NH_2 group or a NHR^{25} group, in which R^{25} is a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl, or

(vi) 3,4-diaminobenzoic acid, or

(vii) combinations thereof; and

(B) oxidatively developing the coloring composition using atmospheric oxygen, an enzyme containing system, or combinations thereof as the sole oxidizing agent.

27. (NEW) The method of claim 26 wherein the pyrimidine derivative is 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine, 2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, or 4-methylamino-2,5,6-tetraminopyrimidine or combinations thereof.

28. (NEW) The method of claim 27 wherein the pyrimidine derivative is 2,4,5,6-tetra-aminopyrimidine.

29. (NEW) The method of claim 26 wherein at least one of R^7 and R^8 of the Formula III is a C_1 to C_4 alkyl group or a C_1 to C_4 hydroxyalkyl group, and wherein R^{20} of the Formula VIII is hydrogen or a C_1 to C_4 alkoxy group.

30. (NEW) The method of claim 26 wherein the component B comprises 1,3-bis(2,4-diaminophenoxypropane), 1,3-bis(2,4-diaminophenylpropane), 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenol, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, or N-(2-hydroxyethyl)-3,4-methylenedioxyaniline or combinations thereof.

REMARKS

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claims 14 to 30 will be pending after entry of the present amendment. Claim 1 is being canceled without prejudice.

Amendment

The specification is being amended on page 23 to delete "lacuna" which is a typographical error.

New Claims 14 to 30 replace original Claims 1 to 13, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
14, 26	page 3, line 24 to page 7, line 19, page 10, line 26 to page 10, line 10, page 21, line 15 to page 22, line 25, page 24, line 25 to page 25, line 3
15, 16, 27, 28	page 7, line 30 to page 8, line 7
17	page 8, lines 11 to 15
18, 29	page 4, line 17 to page 5, line 12, page 6, lines 1 to 22
19, 30	page 8, lines 18 to 28
20	page 8, lines 29 to 32
21	page 9, line 29 to page 10, line 11
22, 23	page 9, lines 3 to 18
24	page 12, lines 22 to 30
25	page 24, line 25 to page 25, line 3

No new matter is added by the new claims or amendments to the specification.

CONCLUSION

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

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Agent for Coloring Keratinaceous Fibers

The invention relates to an agent for dyeing keratin fibers, in particular human hair, which comprises pyrimidine derivatives in combination with special couplers, to the use of this combination as dyeing component in hair dyeing agents, and to a method of dyeing keratin fibers, in particular human hair.

For the dyeing of keratin fibers, e.g. hair, wool or furs, use is generally made either of substantive dyes or oxidation dyes which are formed by oxidative coupling of one or more developer component with one another or with one or more coupler components. Coupler and developer components are also referred to as oxidation dye precursors.

The developer components usually used are primary aromatic amines having a further free or substituted hydroxyl or amino group in the para or ortho position, diaminopyridine derivatives, heterocyclic hydrazones, 4-aminopyrazolone derivatives, and 2,4,5,6-tetraaminopyrimidine and derivatives thereof.

Specific representatives are, for example, p-phenylene-diamine, p-toluylenediamine, 2,4,5,6-tetraaminopyrimidine, p-aminophenol, N,N-bis(2-hydroxyethyl)-p-phenylenediamine, 2-(2,5-diaminophenyl)ethanol, 2-(2,5-diaminophenoxy)ethanol, 1-phenyl-3-carboxyamido-4-aminopyrazol-5-one, 4-amino-3-methylphenol, 2-aminomethyl-4-aminophenol, 2-hydroxymethyl-4-aminophenol, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine and 2,5,6-triamino-4-hydroxypyrimidine.

The coupler components usually used are m-phenylene-diamine derivatives, naphthols, resorcinol and resorcinol derivatives, pyrazolones and m-aminophenols. Particularly suitable as coupler

substances are α-naphthol, 1,5-, 2,7- and 1,7-dihydroxynaphthaline, 5-amino-2-methylphenol, m-aminophenol, resorcinol, resorcinol monomethyl ether, m-phenylenediamine, 2,4-diaminophenoxyethanol, 1-phenyl-3-methylpyrazol-5-one, 2,4-dichloro-3-aminophenol, 1,3-bis(2,4-diaminophenoxy)propane, 2-chlororesorcinol, 4-chlororesorcinol, 2-chloro-6-methyl-3-aminophenol, 2-methylresorcinol and 5-methylresorcinol.

German patent application DE-A1-41 15 148 discloses oxidation dyeing agents which, in a cosmetic carrier, comprise a 2,4,5,6-tetraaminopyrimidine or a 6-hydroxy-2,4-triaminopyridine as oxidation base (developer) and a combination of certain green couplers and violet couplers for producing brilliant and washfast black colorations.

With regard to further customary dye components, reference is made specifically to the "Dermatology" series, published by Ch. Culnan, H. Maibach, Verlag Marcel Dekker Inc., New York, Basle, 1986, vol. 7, Ch. Zviak, The Science of Hair Care, chapter 7, pages 248-250 (substantive dyes), and chapter 8, pages 264-267 (oxidation dyes), and the "European Inventory of Cosmetic Raw Materials", 1996, published by the European Commission, available in diskette format from the Bundesverband der deutschen Industrie- und Handelsunternehmen für Arzneimittel, Reformwaren und Körperpflegemittel e.V., Mannheim.

Although intensive colorations with good fastness properties can be achieved with oxidation dyes, the development of the color, however, generally takes place under the influence of oxidizing agents, such as, for example, H_2O_2, which in some cases can result in damage to the fibers. Furthermore, some oxidation dye precursors or certain mixtures of oxidation dye precursors can occasionally have a sensitizing effect in people with sensitive skin. Although substantive dyes are applied under more moderate conditions, their

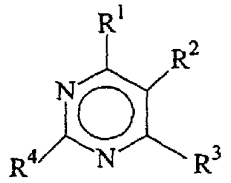
disadvantage is that the colorations frequently have inadequate fastness properties.

It is an object of the present invention to provide a dyeing agent for keratin fibers, in particular human hair, which is oxidizable by atmospheric oxygen, i.e. is not necessarily dependent on oxidizing agents, such as, for example, H_2O_2. The agent should be able to be applied to the fibers in a simple manner and, with regard to depth of color, gray coverage and fastness properties, are at least equal in qualitative terms to otherwise customary oxidation hair dyeing agents. Moreover, the dyeing agents must have no, or only a very low, sensitizing potential. It was a further object to find a dyeing system that allows blue shades to be produced on the keratin fiber by components specifically matched to one another.

Surprisingly, it has now been found that pyrimidine derivatives in combination with special couplers are highly suitable for the dyeing of keratin fibers, even in the absence of oxidizing agents i.e. in the presence of atmospheric oxygen. They produce colorations with excellent brilliance and depth of color and lead to a wide variety of color shades. However, the use of oxidizing agents should not in principle be excluded here.

The invention provides an agent for the dyeing of keratin fibers, in particular human hair, comprising

A) at least one pyrimidine derivative of the general formula I

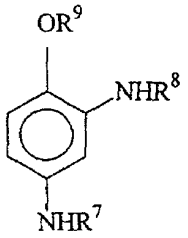


(I)

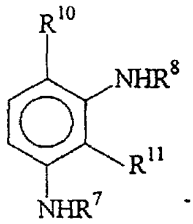
in which R^1, R^2, R^3 and R^4 may be identical or different and are hydrogen, OH, NH_2

or a group NR^5R^6, in which R^5 and R^6 may be identical or different and are C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl having a primary and/or secondary hydroxyl group,
where two of the radicals R^1, R^2, R^3 or R^4 together can form an optionally substituted 5- and 6-membered heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule,
with the proviso that at least two of the radicals R^1, R^2, R^3 or R^4 are a group NH_2 and/or NR^5R^6,

B) at least one compound chosen from the group consisting of
(a) m-phenylene derivatives of the formulae II and III

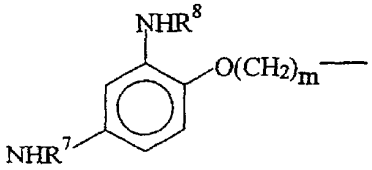


(II)



(III)

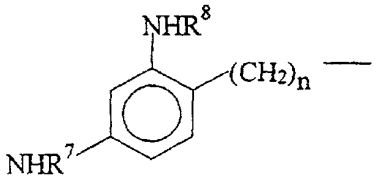
in which R^7 and R^8 may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
R^9 is C_1-C_4-hydroxyalkyl or a radical of the general formula IV



(IV)

in which R^7 and R^8 are as defined above and m is an integer from 1 to 4,

R^{10} is hydrogen or a radical of the general formula V

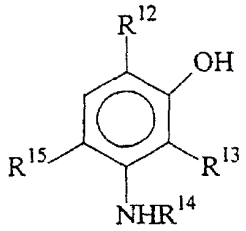


(V)

in which R^7 and R^8 are as defined above and n is an integer from 1 to 4,

R^{11} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,

(b) m-aminophenol derivatives



(VI)

in which R^{12} is hydrogen or C_1-C_4-alkyl,

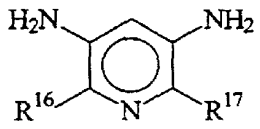
R^{13} is hydrogen, fluorine, chlorine, OCH_3 or C_1-C_4-alkyl,

R^{14} is hydrogen, C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl or OCF_3,

R^{15} is hydrogen, fluorine, chlorine or OCH_3,

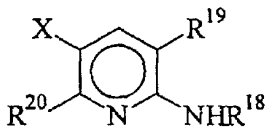
with the provisos that R^{12}, R^{13}, R^{14} and R^{15} are not hydrogen at the same time and that, if R^{12} is methyl, R^{13}, R^{14} and R^{15} are not hydrogen at the same time,

(c) pyridine derivatives of the formulae VII and VIII



(VII)

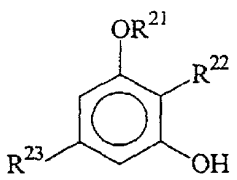
in which R^{16} and R^{17} may be identical or different and are fluorine, chlorine or OCH_3,



(VIII)

in which R^{18} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
R^{19} is OH or NH_2,
R^{20} is hydrogen, C_1-C_4-alkoxy or NH_2,
X is hydrogen or OCH_3,
with the provisos that, if R^{19} is NH_2, R^{18} and R^{20} are not C_1-C_4-alkyl or methoxy respectively at the same time, and if R^{18} is hydrogen, R^{19} and R^{20} are not OH or hydrogen respectively at the same time,

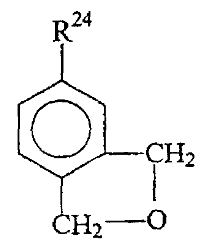
(d) resorcinol derivatives of the formula IX



(IX)

in which R^{21}, R^{22} and R^{23} may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl, with the provisos that R^{21}, R^{22} and R^{23} are not hydrogen at the same time, if R^{21} and R^{23} are hydrogen, R^{22} is not methyl, and if R^{21} is methyl, R^{22} and R^{23} are not hydrogen at the same time,

(e) methylenedioxybenzene derivatives of the formula X



(X)

in which R^{24} is OH, NH_2 or NHR^{25}, in which R^{25} is C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl, and

(f) 3,4-diaminobenzoic acid.

Keratin fibers are to be understood as meaning wool, furs, feathers and, in particular, human hair. In principle, however, the dyes according to the invention may also be used for the dyeing of other natural fibers, such as, for example, cotton, jute, sisal, linen or silk, modified natural fibers, such as, for example, regenerated cellulose, nitro-, alkyl- or hydroxyalkyl- or acetylcellulose, and synthetic fibers, such as, for example, polyamide, polyacrylonitrile, polyurethane and polyester fibers.

The pyrimidine derivatives of the formula I used according to the invention are preferably chosen from the group consisting of 4-hydroxy-2,5,6-triamino-pyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine,

2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, 4-dimethylamino-2,5,6-tetraminopyrimidine. Particular preference is given to using 2,4,5,6-tetraaminopyrimidine, 4-dimethylamino-2,5,6-tetraminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine and 5,6-diamino-2,4-dihydroxypyrimidine.

These substances are known from the literature or are available commercially.

The aforementioned pyrimidine derivatives of the formula I are preferably used in the agents according to the invention in an amount of from 0.03 to 65 mmol, in particular from 1 to 40 mmol, based on 100 g of the total dyeing agent.

Of the compounds of the formula VIII, preference is given to those in which X is hydrogen.

Couplers of component B are preferably chosen from the group 1,3-bis(2,4-diaminophenoxypropane), 1,3-bis(2,4-diaminophenylpropane), 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenyl, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, N-(2-hydroxyethyl)-3,4-methylenedioxyaniline and any mixtures of the above.

The aforementioned compounds of component B can be used in an amount of, in each case, 0.03 to 65 mmol, in particular 1 to 40 mmol, in each case based on 100 g of the total dyeing agent.

In all of the dyeing agents it is also possible to use two or more different pyrimidine derivatives of the formula I together; likewise, it is also possible to use two or more different compounds of component B together. This embodiment also covers the use of substances which represent reaction products of

pyrimidine derivatives of the formula I with said compounds of component B.

The color shades can also be further varied and intensified if one or more compounds chosen from 5,6-dihydroxyindole and its N-substituted C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl derivatives, 5,6-dihydroxyindoline and its N-substituted C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl derivatives and the compounds known as developers, chosen from the group consisting of p-phenylenediamine, p-tolylenediamine, p-aminophenol, 4,4'-diaminodiphenylamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2,(2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 5-aminosalicylic acid, bis(2-hydroxy-5-aminophenyl)methane and 2-(2,5-diaminophenoxy)ethanol are added to the agent according to the invention.

A further preferred developer component is 4-amino-2-((diethylamino)methyl)phenol.

Particularly preferred developer components are, for example, p-phenylenediamine, p-tolylenediamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2,(2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 4-amino-2-((diethylamino)methyl)phenol and bis(2-hydroxy-5-aminophenyl)methane.

In a further preferred embodiment, activated carbonyl compounds and further substances known as developers or couplers are added to the combination according to the invention of components A and B to further modify the color shades.

Examples of activated carbonyl compounds are isatin, 5-chloroisatin, 5-bromoisatin, 6-bromoisatin, 5-nitroisatin, N-hydroxymethylisatin, N-allylisatin, 5-isatinsulfonic acid Na salt, glutaconaldehyde tetrabutylammonium salt, tribase aldehyde,

malonaldehyde bis(dimethyl acetal), 4-hydroxy-3-methoxycinnanaldehyde, 1-piperidinomethylisatin, 1-diethylaminomethylisatin, glutaconaldehyde Na salt, 5-N-methylanilinopentadienyl, 2-chloro-3-hydroxymethylene-1-cyclohexene 1-aldehyde, N-(5-anilino-2,4-pentanedien-1-ylidene)anilinium chloride, trans-β-(2-furyl)acrolein, 2-nitro-1,3-indanedione, dehydroascorbic acid, 2-acetyl-1,3-cyclohexanedione, 7-dimethylamino-2,4,6-heptatrienylidene dimethylammonium perchlorate and 4-formyl-1-methylpyridinium benzenesulfonate.

Examples of couplers which may additionally be present are 3-amino-2-methylamino-6-methoxypyridine, 2-amino-4-(2'-hydroxyethylamino)anisole, α-naphthol, resorcinol, resorcinol monomethyl ether, 4-chlororesorcinol, 2-methylresorcinol, m-aminophenol, 3-N,N-dimethylaminophenol, 5-amino-2-methoxyphenol, 5-amino-2-methylphenol, 3-amino-2,4-dimethylphenol, 3-(N-cyclopentyl)aminophenol, 1,5-, 1,7-, 2,7-dihydroxynaphthalenes, o-aminophenol, 6-hydroxybenzomorpholine, 1-phenyl-3-methylpyrazol-5-one, 2-amino-6-methylphenol, 2,6-dihydroxy-3,4-dimethylpyridine, 4-hydroxyindole, 6-hydroxyindole, 7-hydroxyindole, 4-aminoindole and 2,4-diamino-5-methylphenetole.

The dyeing agent according to the invention represents an air-oxidizable system. In this connection, it is possible to dispense with additional oxidizing agents, e.g. H_2O_2. In some circumstances, however, it may be desirable to add hydrogen peroxide or other oxidizing agents, such as peroxydisulfate or percarbonate, to the agents according to the invention to achieve shades which are paler than keratin fibers to be dyed. Furthermore, in some circumstances, it is possible, in the absence of oxidizing agents, i.e. whether atmospheric oxygen or hydrogen peroxide is used, to establish different color shades. Oxidizing agents are generally used in an amount of from 0.01 to

6% by weight, based on the use solution. An oxidizing agent preferred for human hair is H_2O_2.

Furthermore, it is possible to carry out the oxidation using enzymes. Here, the enzymes can be used either to generate oxidizing percompounds, and to intensify the effect of a small amount of oxidizing agent present. Examples of enzymatic processes are the use of laccases and the intensification of the effect of small amounts (e.g. 1% and less, based on the total agent) of hydrogen peroxide by peroxidases.

In a preferred embodiment, the dyes according to the invention comprise, for the further modification of the color shades, in addition to the compounds present according to the invention, additionally customary substantive dyes, e.g. from the group of nitrophenylenediamines, nitroaminophenols, anthraquinones or indophenols, such as, for example, the compounds known under the international designations or trade names HC Yellow 2, HC Yellow 4, HC Yellow 6, Basic Yellow 57, Disperse Orange 3, HC Red 3, HC Red BN, Basic Red 76, HC Blue 2, Disperse Blue 3, Basic Blue 99, HC Violet 1, Disperse Violet 1, Disperse Violet 4, Disperse Black 9, Basic Brown 16 and Basic Brown 17, and also picramic acid, 2-amino-6-chloro-4-nitrophenol, 4-amino-2-nitrodiphenylamine-2'-carboxylic acid, 6-nitro-1,2,3,4-tetrahydroquinoxaline, 4-N-ethyl-1,4-bis(2'-hydroxyethylamino)-2-nitrobenzene hydrochloride and 1-methyl-3-nitro-4-(2'-hydroxyethyl)aminobenzene. The inventive agents according to this embodiment preferably comprise the substantive dyes in an amount of from 0.01 to 20% by weight, based on the total dyeing agent.

Furthermore, the preparations according to the invention can also comprise naturally occurring dyes such as, for example, henna red, henna neutral, henna black, camomile blossom, sandalwood, black tea, buckthorn bark, sage, logwood, madder root, catechu, sedre and alkanna root.

It is not necessary for the oxidation dye precursors or the optionally present substantive dyes to each represent uniform compounds. Rather, it is possible that, as a result of the preparation processes for the individual dyes, further components are present in minor amounts in the dyeing agents according to the invention, provided these do not adversely impair the dyeing result, or have to be excluded for other reasons, e.g. toxicological reasons.

The dyeing agents according to the invention produce intensive colorations even at physiologically compatible temperatures of less than 45°C. They are therefore particularly suitable for the dyeing of human hair. For use on human hair, the dyeing agents can usually be incorporated into a hydrous cosmetic carrier. Suitable hydrous cosmetic carriers are e.g. creams, emulsions, gels and also surfactant-containing foaming solutions such as e.g. shampoos or other preparations which are suitable for use on the keratin fibers. If necessary, it is also possible to incorporate the dyeing agents into anhydrous carriers.

Furthermore, the dyeing agents according to the invention can comprise all active ingredients, additives and auxiliaries known in such preparations. In many cases, the dyeing agents comprise at least one surfactant, where, in principle, both anionic and also zwitterionic, ampholytic, nonionic and cationic surfactants are suitable. However, in many cases it has proven advantageous to choose the surfactants from anionic, zwitterionic or nonionic surfactants.

Suitable anionic surfactants in preparations according to the invention are all anionic surface-active substances suitable for use on the human body. These are characterized by a solubilizing anionic group, such as, for example, a carboxylate, sulfate, sulfonate or phosphate group and a lipophilic alkyl group having about 10 to 22 carbon atoms. Additionally, glycol or polyglycol ether groups, ester, ether and

amide groups and hydroxyl groups may be present in the molecule. Examples of suitable anionic surfactants are, in each case in the form of the sodium, potassium or ammonium and the mono-, di- and trialkanolammonium salts having 2 or 3 carbon atoms in the alkanol group,

- linear fatty acids having 10 to 22 carbon atoms (soaps)
- ether carboxylic acids of the formula $R-O-(CH_2-CH_2O)_x-CH_2-COOH$, in which R is a linear alkyl group having 10 to 22 carbon atoms and x = 0 or 1 to 16,
- acyl sarcosides having 10 to 18 carbon atoms in the acyl group,
- acyl taurides having 10 to 18 carbon atoms in the acyl group,
- acyl isethionates having 10 to 18 carbon atoms in the acyl group,
- sulfosuccinic mono- and dialkyl esters having 8 to 18 carbon atoms in the alkyl group and sulfosuccinic monoalkylpolyoxyethyl esters having 8 to 18 carbon atoms in the alkyl group and 1 to 6 oxyethyl groups,
- linear alkanesulfonates having 12 to 18 carbon atoms,
- linear alpha-olefinsulfonates having 12 to 18 carbon atoms,
- alpha-sulfo fatty acid methyl esters of fatty acids having 12 to 18 carbon atoms,
- alkyl sulfates and alkylpolyglycol ether sulfates of the formula $R-O(CH_2-CH_2O)_x-SO_3H$, in which R is a preferably linear alkyl group having 10 to 18 carbon atoms and x = 0 or 1 to 12,
- mixtures of surface-active hydroxysulfonates according to DE-A-37 25 030,
- sulfated hydroxyalkyl polyethylene and/or hydroxyalkylene propylene glycol ethers according to DE-A-37 23 354,

- sulfonates of unsaturated fatty acids having 12 to 24 carbon atoms and 1 to 6 double bonds according to DE-A-39 26 344,
- esters of tartaric acid and citric acid with alcohols, which represent addition products of approximately 2 to 15 molecules of ethylene oxide and/or propylene oxide to fatty alcohols having 8 to 22 carbon atoms.

Preferred anionic surfactants are alkyl sulfates, alkylpolyglycol ether sulfates and ether carboxylic acids having 10 to 18 carbon atoms in the alkyl group and up to 12 glycol ether groups in the molecule, and in particular salts of saturated and in particular unsaturated C_8-C_{22}-carboxylic acids, such as oleic acid, stearic acid, isostearic acid and palmitic acid.

Zwitterionic surfactants is the term used for those surface-active compounds which carry at least one quaternary ammonium group and at least one $-COO^{(-)}$- or $-SO_3^{(-)}$ group in the molecule. Particularly suitable zwitterionic surfactants are the betaines, such as the N-alkyl-N,N-dimethylammonium glycinates, for example the cocoalkyldimethylammonium glycinate, N-acyl-amminopropyl-N,N-dimethylammonium glycinates, for example the cocoacylaminopropyldimethylammonium glycinate, and 2-alkyl-3-carboxymethyl-3-hydroxy-ethylimidazolines having in each case 8 to 18 carbon atoms in the alkyl or acyl group, and cocoacylaminoethyl hydroxyethylcarboxymethylglycinate. A preferred zwitterionic surfactant is the fatty acid amide derivative known under the CTFA name Cocamidopropyl Betaine.

Ampholytic surfactants are understood as meaning those surface-active compounds which, apart from a C_{8-18}-alkyl or -acyl group in the molecule, contain at least one free amino group and at least one -COOH or -SO_3H group and are capable of forming internal salts. Examples of suitable ampholytic surfactants are

N-alkylglycines, N-alkylpropionic acids, N-alkylaminobutyric acids, N-alkylaminodipropionic acids, N-hydroxyethyl-N-alkylamidopropylglycines, N-alkyltaurines, N-alkylsarcosines, 2-alkylaminopropionic acids and alkylaminoacetic acids having in each case about 8 to 18 carbon atoms in the alkyl group. Particularly preferred ampholytic surfactants are N-cocoalkylaminopropionate, cocoacylaminoethylaminopropionate and C_{12-18}-acylsarcosine.

Nonionic surfactants comprise, as hydrophilic group, e.g. a polyol group, a polyalkylene glycol ether group or a combination of polyol and polyglycol ether group. Such compounds are, for example,

- addition products of 2 to 30 mol of ethylene oxide and/or 0 to 5 mol of propylene oxide to linear fatty alcohols having 8 to 22 carbon atoms, to fatty acids having 12 to 22 carbon atoms and to alkyl phenols having 8 to 15 carbon atoms in the alkyl group,
- C_{12-22}-fatty acid mono- and diesters of addition products of from 1 to 30 mol of ethylene oxide to glycerol,
- C_{8-22}-alkyl mono- and oligoglycosides and ethoxylated analogs thereof,
- addition products of from 5 to 60 mol of ethylene oxide to castor oil and hydrogenated castor oil,
- addition products of ethylene oxide to sorbitan fatty acid esters
- addition products of ethylene oxide to fatty acid alkanolamides.

Examples of the cationic surfactants to be used in the hair-treatment agents according to the invention are, in particular, quaternary ammonium compounds. Preference is given to ammonium halides, such as alkyltrimethylammonium chlorides, dialkyldimethyl-

ammonium chlorides and trialkylmethylammonium chlorides, e.g. cetyltrimethylammonium chloride, stearyltrimethylammonium chloride, distearyldimethylammonium chloride, lauryldimethylammonium chloride, lauryldimethylbenzylammonium chloride and tricetylmethylammonium chloride. Further cationic surfactants which can be used according to the invention are the quaternized protein hydrolysates.

Likewise suitable for the invention are cationic silicone oils, such as, for example, the commercially available products Q2-7224 (manufacturer: Dow Corning; a stabilized trimethylsilylamodimethicone), Dow Corning 949 emulsion (comprising a hydroxylamino-modified silicone, which is also referred to as amodimethicone), SM-2059 (manufacturer: General Electric), SLM-55067 (manufacturer: Wacker) and Abil®-Quat 3270 and 3272 (manufacturer: Th. Goldschmidt; diquaternary polydimethylsiloxanes, Quaternium-80).

Alkylamidoamines, in particular fatty acid amidoamines, such as stearylamidopropyldimethylamine obtainable under the name Tego Amid®S 18, are distinguished not only by a good conditioning action, but specifically by their good biodegradability.

Likewise very biodegradable are quaternary ester compounds, "ester quats", such as the methylhydroxyalkyldialkoyloxyalkylammonium methosulfates sold under the trade name Stepantex®.

An example of a quaternary sugar derivative which can be used as cationic surfactant is the commercial product Glucquat® 100, according to CTFA nomenclature a "Lauryl Methyl Gluceth-10 Hydroxypropyl Dimonium Chloride".

The compounds containing alkyl groups which are used as surfactants may each be uniform substances. However, it is generally preferred to start from natural vegetable or animal raw materials for the preparation of these substances, thus giving substance

mixtures having varying alkyl chain lengths depending on the respective raw material.

In the case of the surfactants which represent additional products of ethylene and/or propylene oxide to fatty alcohols or derivatives of these addition products, it is possible to use either products with a "normal" homolog distribution, or those with a narrowed homolog distribution. "Normal" homolog distribution is understood as meaning here mixtures of homologs obtained during the reaction of fatty alcohol and alkylene oxide using alkali metals, alkali metal hydroxides or alkali metal alkoxides as catalysts. Narrowed homolog distributions are, by contrast, obtained if, for example, hydrotalcites, alkaline earth metal salts of ether carboxylic acids, alkaline earth metal oxides, hydroxides or alkoxides are used as catalysts. The use of products having narrowed homolog distribution may be preferable.

Further active ingredients, auxiliaries and additives are, for example,

- nonionic polymers such as, for example, vinylpyrrolidone/vinyl acrylate copolymers, polyvinylpyrrolidone and vinylpyrrolidone/vinyl acetate copolymers and polysiloxanes,
- cationic polymers, such as quaternized cellulose ethers, polysiloxanes containing quaternary groups, dimethyldiallylammonium chloride polymers, acrylamide-dimethyldiallylammonium chloride copolymers, dimethylaminoethyl methacrylate-vinylpyrrolidone copolymers quaternized with diethyl sulfate, vinylpyrrolidone-imidazolinium methochloride copolymers and quaternized polyvinyl alcohol,
- zwitterionic and amphoteric polymers such as, for example, acrylamidopropyltrimethylammonium chloride/acrylate copolymers and octylacryl-amide/methyl methacrylate/tert-butylaminoethyl

methacrylate/2-hydroxypropyl methacrylate copolymers,

- anionic polymers such as, for example, polyacrylic acids, crosslinked polyacrylic acids, vinyl acetate/crotonic acid copolymers, vinyl-pyrrolidone/vinyl acrylate copolymers, vinyl acetate/butyl maleate/isobornyl acrylate copolymers, methyl vinyl ether/maleic anhydride copolymers and acrylic acid/ethyl acrylate/N-tert-butylacrylamide terpolymers,
- thickeners, such as agar agar, guar gum, alginates, xanthan gum, gum arabic, karaya gum, carob bean flour, linseed gums, dextrans, cellulose derivatives, e.g. methylcellulose, hydroxyalkylcellulose and carboxymethylcellulose, starch fractions and derivatives such as amylose, amylopectin and dextrins, clays such as, for example, bentonite or fully synthetic hydrocolloids such as, for example, polyvinyl alcohol,
- structurants, such glucose and maleic acid,
- hair-conditioning compounds, such as phospholipids, for example soya lecithin, egg lecithin and cephalins, and silicone oils,
- protein hydrolysates, in particular elastin, collagen, keratin, milk protein, soya protein and wheat protein hydrolysates, condensation products thereof with fatty acids, and quaternized protein hydrolysates,
- perfume oils, dimethyl isosorbide and cyclodextrins,
- solubility promoters, such as ethanol, isopropanol, ethylene glycol, propylene glycol, glycerol and diethylene glycol,
- antidandruff agents, such as Piroctone Olamine and Zinc Omadine,
- further substances for adjusting the pH,

- active ingredients, such as panthenol, pantothenic acid, allantoin, pyrrolidonecarboxylic acids and salts thereof, plant extracts and vitamins,
- cholesterol,
- light protection agents,
- consistency regulators, such as sugar esters, polyol esters or polyol alkyl ethers,
- fats and waxes, such as spermaceti, beeswax, montan wax, paraffins, fatty alcohols and fatty acid esters,
- fatty acid alkanolamides,
- complexing agents, such as EDTA, NTA and phosphonic acids,
- swelling and penetration substances, such as glycerol, propylene glycol monoethyl ether, carbonates, hydrogencarbonates, guanidines, ureas, and primary, secondary and tertiary phosphates, imidazoles, tannins, pyrrole,
- opacifiers, such as latex,
- pearlizing agents, such as ethylene glycol mono- and distearate,
- propellants, such as propane/butane mixtures, N_2O, dimethyl ether, CO_2 and air, and
- antioxidants.

The constituents of the hydrous carrier are used for the preparation of the dyeing agents according to the invention in amounts customary for this purpose; e.g. emulsifiers are used in concentrations of from 0.5 to 30% by weight, and thickeners are used in concentrations of from 0.1 to 25% by weight, of the total dyeing agent.

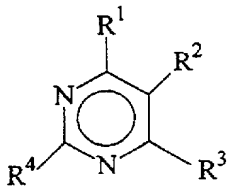
For the dyeing result, it may be advantageous to add ammonium or metal salts to the dyeing agents. Suitable metal salts are e.g. formates, carbonates, halides, sulfates, butyrates, valerates, caproates, acetates, lactates, glycolates, tartrates, citrates, gluconates, propionates, phosphates and phosphonates of alkali metals, such as potassium, sodium or lithium,

alkaline earth metals, such as magnesium, calcium, strontium or barium, or of aluminum, manganese, iron, cobalt, copper or zinc, preference being given to sodium acetate, lithium bromide, calcium bromide, calcium gluconate, zinc chloride, zinc sulfate, magnesium chloride, magnesium sulfate, ammonium carbonate, chloride and acetate. These salts are preferably present in an amount of from 0.03 to 65 mmol, in particular from 1 to 40 mmol, based on 100 g of the total dyeing agent.

The pH of the ready-to-use dyeing preparations is usually between 2 and 11, preferably between 5 and 9.

The present invention further provides for the use of a combination of

A) at least one pyrimidine derivative of the general formula I



(I)

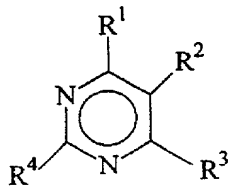
in which R^1, R^2, R^3 and R^4 may be identical or different and are hydrogen, OH, NH_2 or a group NR^5R^6, in which R^5 and R^6 may be identical or different and are C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl having a primary and/or secondary hydroxyl group, where two of the radicals R^1, R^2, R^3 or R^4 together can form an optionally substituted 5- and 6-membered heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule,
with the proviso that at least two of the radicals R^1, R^2, R^3 or R^4 are a group NH_2 and/or NR^5R^6,

B) at least one compound chosen from the group consisting of the (a) m-phenylenediamine derivatives of the general formulae II or III, (b) m-aminophenol derivatives of the general formula VI, (c) pyridine derivatives of the formulae VII or VIII, (d) resorcinol derivatives of the formula IX, (e) methyldioxybenzene derivatives of the formula X or (f) 3,4-diaminobenzoic acid, which are shown above,

for dyeing keratin fibers.

The present invention also further provides a method of dyeing keratin fibers, in particular human hair, in which a dyeing agent comprising

A) at least one pyrimidine derivative of the general formula I,



(I)

in which R^1, R^2, R^3 and R^4 may be identical or different and are hydrogen, OH, NH_2 or a group NR^5R^6, in which R^5 and R^6 may be identical or different and are C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl having a primary and/or secondary hydroxyl group, where two of the radicals R^1, R^2, R^3 or R^4 together can form an optionally substituted 5- and 6-membered heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule,
with the proviso that at least two of the radicals R^1, R^2, R^3 or R^4 are a group NH_2 and/or NR^5R^6,

B) at least one compound chosen from the group consisting of the (a) m-phenylenediamine derivatives of the general formulae II or III, (b) m-aminophenol derivatives of the general formula VI, (c) pyridine derivatives of the formulae VII or VIII, (d) resorcinol derivatives of the formula IX, (e) methyldioxybenzene derivatives of the formula X or (f) 3,4-diaminobenzoic acid,

and customary cosmetic ingredients, is applied to the keratin fibers, left on the fibers for a while, usually about 30 minutes, and then rinsed out again or washed out using a shampoo.

The pyrimidine derivatives of the formula I and the compounds of component B can either be applied to the hair simultaneously or one after the other, it being unimportant which of the two components is applied first. If it is necessary to achieve a certain color shade, any oxidizing agent used is also applied in this stage together with the other components, or subsequently. The optionally present ammonium or metal salts may be added to the first or the second component. There may be an interval of up to 30 minutes between application of the first component and that of the second component. Pretreatment of the fibers with the salt solution is also possible.

Examples

Hair dyeing agents according to the invention were [lacuna] in the form of a hair dyeing cream emulsion of the composition given in Table 1.

Table 1

	1	2	3	4	5	6	7
Component	% by wt.						
C_{12}-C_{14}-fatty alcohol + 2 EO sulfate, Na salt, 28% strength solution	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Cocoamidopropylbetaine, 30% strength	12.5	12.5	12.5	12.5	12.5	12.5	12.5
C_{10}-C_{18} fatty alcohol	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Tallow fatty alcohol	8.5	8.5	8.5	8.5	8.5	8.5	8.5
C_{16}-C_{18} fatty alcohol + 20 EO	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Ammonium sulfate	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Sodium sulfate	0.1	0.1	0.1	0.1	0.1	0.1	0.1
4-Hydroxy-2,5,6-tri-aminopyrimidine sulfate	2.4	2.4	2.4	2.4	2.4	2.4	2.4
2,4-Diaminophenoxy-ethanol dihydrochloride	2.4	-	-	-	-	-	-
3,5-Diamino-2,6-di-methoxypyridine dihydrochloride	-	2.4	-	-	-	-	-
1,3-bis(2,4-Diamino-phenoxy)propane tetra-hydrochloride	-	-	4.7	2.12	1.18	-	-
N-Allylisatin	-	-	-	0.19	0.94	-	-
1,10-bis(2,5-Diamino-phenyl)-1,4,7-10-tetra-oxydecane tetrahydro-chloride	-	-	-	1.02	5.1	-	-
3-Amino-2-chloro-6-methylphenol	-	-	-	-	-	1.58	-
3,4-Methylenedioxyphenol	-	-	-	-	-	-	1.38
Water	ad 100						

The individual constituents were mixed together at 70°C and, after cooling, adjusted to a pH of 9.5 with NaOH.

Using the compositions given in Table 1, colorations were carried out using H_2O_2 as oxidizing agent and without oxidizing agent, i.e. by air oxidation.

For the oxidative development of the coloration using H_2O_2, the compositions shown in Table 1 were mixed with 12% strength hydrogen peroxide in the ratio 1:1. In the case of air oxidation, the compositions shown in Table 1 were mixed with water prior to use in the ratio 1:1.

The application mixture was applied to approximately 15 cm-long tresses of standardized, 90% gray human hair which has not been pretreated in any particular way, and left there for 30 minutes at 27°C. When the dyeing process was complete, the hair was rinsed, washed with a customary shampoo and then dried. The coloring results are shown in Table 2.

Table 2

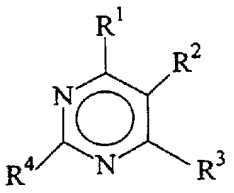
	Color shade	
Formulation No.	H_2O_2 oxidation	Air oxidation
1	Deep blue-violet	Deep blue-violet
2	Reddish mid-brown	Reddish mid-brown
3	Mid-dark brown	Mid-dark brown
4	-	Dark brown
5	-	Black
6	Gray magenta	Rich Bordeaux
7	Pale orange	Sand-colored

The dyeing results show that the agents according to the invention produce excellent coloring results both with and without the addition of oxidizing agents. Similar colorations are obtained if, in example 7, the

enzyme system glucose-oxidase/glucose/peroxidase or the enzyme system uricase/uric acid/peroxidase is used as oxidizing agent at pH = 8.5.

Patent claims

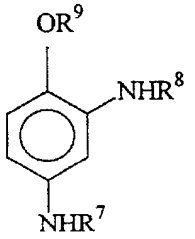
1. An agent for dyeing keratin fibers, comprising
A) at least one pyrimidine derivative of the general formula I



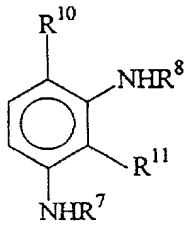
(I)

in which R^1, R^2, R^3 and R^4 may be identical or different and are hydrogen, OH, NH_2 or a group NR^5R^6, in which R^5 and R^6 may be identical or different and are C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl having a primary and/or secondary hydroxyl group,
where two of the radicals R^1, R^2, R^3 or R^4 together can form an optionally substituted 5- and 6-membered heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule,
with the proviso that at least two of the radicals R^1, R^2, R^3 or R^4 are a group NH_2 and/or NR^5R^6,

B) at least one compound chosen from the group consisting of
(a) m-phenylene derivatives of the formulae II and III

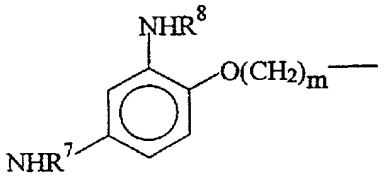


(II)



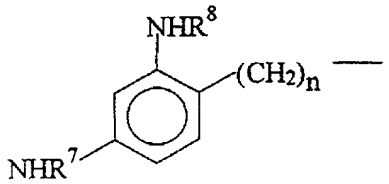
(III)

in which R^7 and R^8 may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
R^9 is C_1-C_4-hydroxyalkyl or a radical of the general formula IV



(IV)

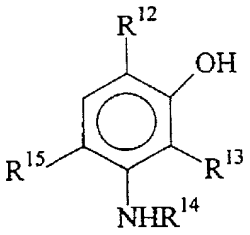
in which R^7 and R^8 are as defined above and m is an integer from 1 to 4,
R^{10} is hydrogen or a radical of the general formula V



(V)

in which R^7 and R^8 are as defined above and n is an integer from 1 to 4,
R^{11} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,

(b) m-aminophenol derivatives

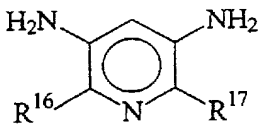


(VI)

in which R^{12} is hydrogen or C_1-C_4-alkyl,
R^{13} is hydrogen, fluorine, chlorine, OCH_3 or C_1-C_4-alkyl,
R^{14} is hydrogen, C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl or OCF_3,
R^{15} is hydrogen, fluorine, chlorine or OCH_3,

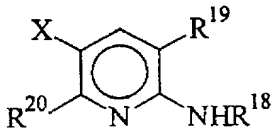
with the provisos that R^{12}, R^{13}, R^{14} and R^{15} are not hydrogen at the same time and that, if R^{12} is methyl, R^{13}, R^{14} and R^{15} are not hydrogen at the same time,

(c) pyridine derivatives of the formulae VII and VIII



(VII)

in which R^{16} and R^{17} may be identical or different and are fluorine, chlorine or $-OCH_3$,



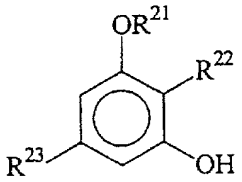
(VIII)

in which R^{18} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,

R^{19} is OH or NH_2,
R^{20} is hydrogen, C_1-C_4-alkoxy or NH_2,
X is hydrogen or OCH_3,

with the provisos that, if R^{19} is NH_2, R^{18} and R^{20} are not C_1-C_4-alkyl or methoxy respectively at the same time, and if R^{18} is hydrogen, R^{19} and R^{20} are not OH or hydrogen respectively at the same time,

(d) resorcinol derivatives of the formula IX

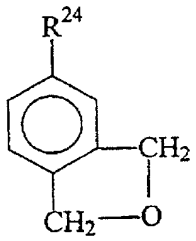


(IX)

in which R^{21}, R^{22} and R^{23} may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,

with the provisos that R^{21}, R^{22} and R^{23} are not hydrogen at the same time, if R^{21} and R^{23} are hydrogen, R^{22} is not methyl, and if R^{21} is methyl, R^{22} and R^{23} are not hydrogen at the same time,

(e) methylenedioxybenzene derivatives of the formula X



(X)

in which R^{24} is OH, NH_2 or NHR^{25}, in which R^{25} is C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl, and

(f) 3,4-diaminobenzoic acid.

2. The agent as claimed in claim 1, characterized in that 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-2,5,6-triaminopyrimidine, 2,4,5,6-tetraaminopyrimidine, 5,6-diamino-2,4-dihydroxypyrimidine, 2,4-diamino-5,6-dihydroxypyrimidine, 4-dimethylamino-2,5,6-tetraminopyrimidine and any mixtures thereof are present as pyrimidine derivatives of the formula I.

3. The agent as claimed in claim 1 or 2, characterized in that the pyrimidine derivatives of the formula I are present in an amount of from 0.03 to 65 mmol, in particular from 1 to 40 mmol, based on 100 g of the total dyeing agent.

4. The agent as claimed in any of claims 1 to 3, characterized in that the compounds of component B are chosen from the group 1,3-bis(2,4-diaminophenoxypropane), 1,3-bis(2,4-diaminophenylpropane), 2,4-diaminophenoxyethanol, 2,6-bis(2'-hydroxyethylamino)toluene, 3-amino-2-chloro-6-methylphenyl, 5-amino-4-chloro-2-methylphenol, 2,4-dichloro-3-aminophenol, 3,5-diamino-2,6-dimethoxypyridine, 5-methylresorcinol, 2,5-dimethylresorcinol, 3,4-methylenedioxyphenol, 3,4-methylenedioxyaniline, N-(2-hydroxyethyl)-3,4-methylenedioxyaniline and any mixtures thereof.

5. The agent as claimed in any of claims 1 to 4, characterized in that the compounds of component B are present in an amount of, in each case, from 0.03 to 65 mmol, in particular from 1 to 40 mmol, in each case based on 100 g of the total dyeing agent.

6. The agent as claimed in any of claims 1 to 5, characterized in that at least one activated

carbonyl compound chosen from the group consisting of isatin, 5-chloroisatin, 5-bromoisatin, 6-bromoisatin, 5-nitroisatin, N-hydroxymethylisatin, N-allylisatin, 5-isatinsulfonic acid Na salt, glutaconaldehyde tetrabutylammonium salt, tribase aldehyde, malonaldehyde bis(dimethyl acetal), 4-hydroxy-3-methoxycinnanaldehyde, 1-piperidinomethylisatin, 1-diethylaminomethylisatin, glutaconaldehyde Na salt, 5-N-methylanilinopentadienyl, 2-chloro-3-hydroxymethylene-1-cyclohexene 1-aldehyde, N-(5-anilino-2,4-pentanedien-1-ylidene)anilinium chloride, trans-β-(2-furyl)-acrolein, 2-nitro-1,3-indanedione, dehydroascorbic acid, 2-acetyl-1,3-cyclohexanedione, 7-dimethylamino-2,4,6-heptatrienylidene dimethylammonium perchlorate and 4-formyl-1-methylpyridinium benzenesulfonate.

7. The agent as claimed in any of claims 1 to 6, characterized in that one or more compounds chosen from 5,6-dihydroxyindole and its N-substituted C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl derivatives, 5,6-dihydroxyindoline and its N-substituted C_1-C_4-alkyl and C_1-C_4-hydroxyalkyl derivatives and the compounds known as developers, chosen from the group consisting of p-phenylenediamine, p-tolylenediamine, p-aminophenol, 4,4'-diaminodiphenylamine, 1,10-bis(2,5-diaminophenyl)-1,4,7,10-tetraoxydecane, 2,(2'-hydroxyethyl)-p-phenylenediamine, 2,6-dichloro-4-aminophenol, N,N-bis(2'-hydroxyethyl)-p-phenylenediamine, 3-methyl-4-aminophenol, 2-aminomethyl-4-aminophenol, 5-aminosalicylic acid, bis(2-hydroxy-5-aminophenyl)methane, 2-(2,5-diaminophenoxy)ethanol are also added.

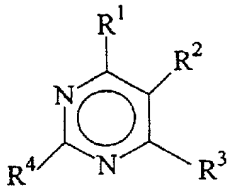
8. The agent as claimed in any of claims 1 to 7, characterized in that it comprises anionic, zwitterionic or nonionic surfactants.

9. The agent as claimed in any of claims 1 to 8, characterized in that it is an air-oxidizable dyeing system.

10. The agent as claimed in any of claims 1 to 8, characterized in that [lacuna] comprises oxidizing agents chosen from the group H_2O_2, peroxydisulfate and percarbonate.

11. The agent as claimed in any of claims 1 to 8, characterized in that it is an enzymatic dyeing system.

12. The use of a combination of
A) at least one pyrimidine derivative of the general formula I

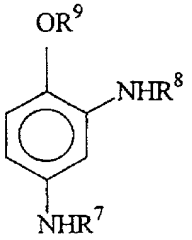


(I)

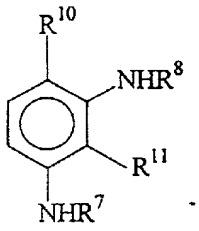
in which R^1, R^2, R^3 and R^4 may be identical or different and are hydrogen, OH, NH_2 or a group NR^5R^6, in which R^5 and R^6 may be identical or different and are C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl having a primary and/or secondary hydroxyl group,
where two of the radicals R^1, R^2, R^3 or R^4 together can form an optionally substituted 5- and 6-membered heterocycle containing one or two

nitrogen and/or oxygen atom(s) in the molecule,
with the proviso that at least two of the radicals R^1, R^2, R^3 or R^4 are a group NH_2 and/or NR^5R^6,

B) at least one compound chosen from the group consisting of
(a) m-phenylene derivatives of the formulae II and III

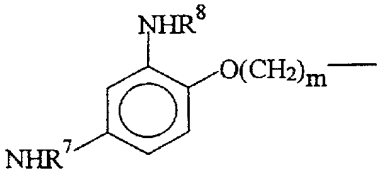


(II)



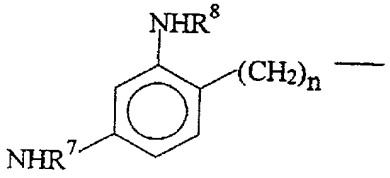
(III)

in which R^7 and R^8 may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
R^9 is C_1-C_4-hydroxyalkyl or a radical of the general formula IV



(IV)

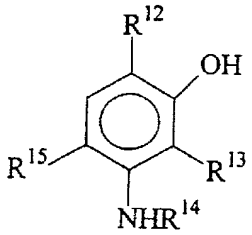
in which R^7 and R^8 are as defined above and m is an integer from 1 to 4,
R^{10} is hydrogen or a radical of the general formula V



(V)

in which R^7 and R^8 are as defined above and n is an integer from 1 to 4,
R^{11} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,

(b) m-aminophenol derivatives

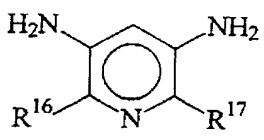


(VI)

in which R^{12} is hydrogen or C_1-C_4-alkyl,
R^{13} is hydrogen, fluorine, chlorine, OCH_3 or C_1-C_4-alkyl,
R^{14} is hydrogen, C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl or OCF_3,
R^{15} is hydrogen, fluorine, chlorine or OCH_3,

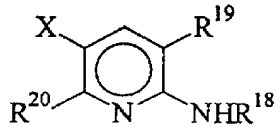
with the provisos that R^{12}, R^{13}, R^{14} and R^{15} are not hydrogen at the same time and that, if R^{12} is methyl, R^{13}, R^{14} and R^{15} are not hydrogen at the same time,

(c) pyridine derivatives of the formulae VII and VIII



(VII)

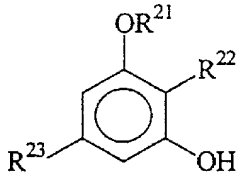
in which R^{16} and R^{17} may be identical or different and are fluorine, chlorine or OCH_3,



(VIII)

in which R^{18} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
R^{19} is OH or NH_2,
R^{20} is hydrogen, C_1-C_4-alkoxy or NH_2,
X is hydrogen or OCH_3,
with the provisos that, if R^{19} is NH_2, R^{18} and R^{20} are not C_1-C_4-alkyl or methoxy respectively at the same time, and if R^{18} is hydrogen, R^{19} and R^{20} are not OH or hydrogen respectively at the same time,

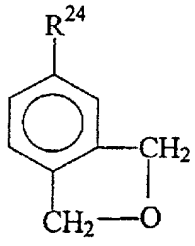
(d) resorcinol derivatives of the formula IX



(IX)

in which R^{21}, R^{22} and R^{23} may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
with the provisos that R^{21}, R^{22} and R^{23} are not hydrogen at the same time, if R^{21} and R^{23} are hydrogen, R^{22} is not methyl, and if R^{21} is methyl, R^{22} and R^{23} are not hydrogen at the same time,

(e) methylenedioxybenzene derivatives of the formula X



(X)

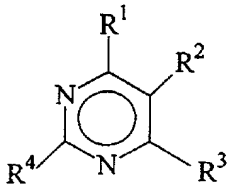
in which R^{24} is OH, NH_2 or NHR^{25}, in which R^{25} is C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl, and

(f) 3,4-diaminobenzoic acid,

for dyeing keratin fibers.

13. A method of dyeing keratin fibers, in particular human hair, in which a dyeing agent comprising

A) at least one pyrimidine derivative of the general formula I



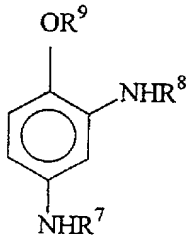
(I)

in which R^1, R^2, R^3 and R^4 may be identical or different and are hydrogen, OH, NH_2 or a group NR^5R^6, in which R^5 and R^6 may be identical or different and are C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl having a primary and/or secondary hydroxyl group,
where two of the radicals R^1, R^2, R^3 or R^4 together can form an optionally substituted 5- and 6-membered

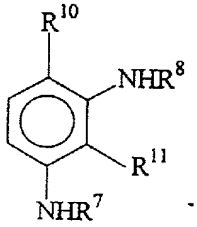
heterocycle containing one or two nitrogen and/or oxygen atom(s) in the molecule,
with the proviso that at least two of the radicals R^1, R^2, R^3 or R^4 are a group NH_2 and/or NR^5R^6,

B) at least one compound chosen from the group consisting of

(a) m-phenylene derivatives of the formulae II and III



(II)

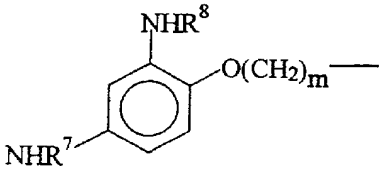


(III)

in which

R^7 and R^8 may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,

R^9 is C_1-C_4-hydroxyalkyl or a radical of the general formula IV

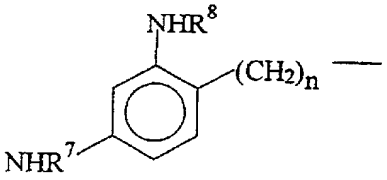


(IV)

in which

R^7 and R^8 are as defined above and m is an integer from 1 to 4,

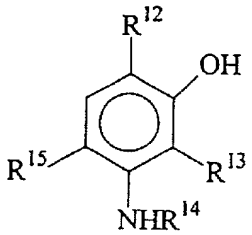
R^{10} is hydrogen or a radical of the general formula V



(V)

in which
R^7 and R^8 are as defined above and n is an integer from 1 to 4,
R^{11} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,

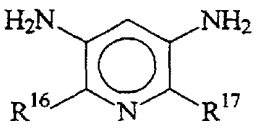
(b) m-aminophenol derivatives



(VI)

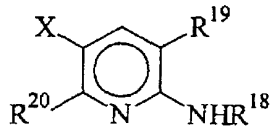
in which
R^{12} is hydrogen or C_1-C_4-alkyl,
R^{13} is hydrogen, fluorine, chlorine, OCH_3 or C_1-C_4-alkyl,
R^{14} is hydrogen, C_1-C_4-alkyl, C_1-C_4-hydroxyalkyl or OCF_3,
R^{15} is hydrogen, fluorine, chlorine or OCH_3,
with the provisos that R^{12}, R^{13}, R^{14} and R^{15} are not hydrogen at the same time and that, if R^{12} is methyl, R^{13}, R^{14} and R^{15} are not hydrogen at the same time,

(c) pyridine derivatives of the formulae VII and VIII



(VII)

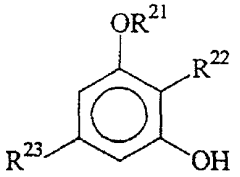
in which
R^{16} and R^{17} may be identical or different and are fluorine, chlorine or $-OCH_3$,



(VIII)

in which R^{18} is hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
R^{19} is OH or NH_2,
R^{20} is hydrogen, C_1-C_4-alkoxy or NH_2,
X is hydrogen or OCH_3,
with the provisos that, if R^{19} is NH_2, R^{18} and R^{20} are not C_1-C_4-alkyl or methoxy respectively at the same time, and if R^{18} is hydrogen, R^{19} and R^{20} are not OH or hydrogen respectively at the same time,

(d) resorcinol derivatives of the formula IX

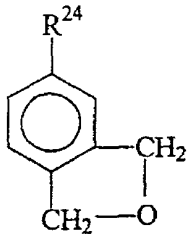


(IX)

in which
R^{21}, R^{22} and R^{23} may be identical or different and are hydrogen, C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl,
with the provisos that R^{21}, R^{22} and R^{23} are not hydrogen at the same time, if R^{21} and R^{23} are

hydrogen, R^{22} is not methyl, and if R^{21} is methyl, R^{22} and R^{23} are not hydrogen at the same time,

(e) methylenedioxybenzene derivatives of the formula X



(X)

in which

R^{24} is OH, NH_2 or NHR^{25}, in which R^{25} is C_1-C_4-alkyl or C_1-C_4-hydroxyalkyl, and

(f) 3,4-diaminobenzoic acid,

and customary cosmetic ingredients, is applied to the keratin fibers, left on the fibers for a while, usually about 30 minutes, and then rinsed out again or washed out using a shampoo.

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PTO/SB/01 (6-95)
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Type a plus sign (+) inside this box → ☐

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Rev. 6/95

U.S. Department of Commerce
Patent and Trademark Office

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket Number	H 3294 PCT/US
First Named Inventor	Hoeffkes, Horst
COMPLETE IF KNOWN	
Application Number	
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:
My residence, post office address, and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

AGENT FOR COLORING KERATINACEOUS FIBERS

(Title of the Invention)

the specification of which
☐ is attached hereto
OR
☒ was filed on (MM/DD/YYYY) 12/14/1999 as United States Application Number or PCT International Application Number PCT/EP99/09901 and was amended on (MM/DD/YYYY) (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
198 59 800.9	Germany	12/23/1998	☐	☐	☒

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	
		☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

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Type a plus sign (+) inside this box → ☐

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U.S. Department of Commerce
Patent and Trademark Office

DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket Number	H 3294 PCT/US
First Named Inventor	Hoeffkes, Horst
COMPLETE IF KNOWN	
Application Number	
Filing Date	
Group Art Unit	
Examiner Name	

As a below named inventor, I hereby declare that:
My residence, post office address, and citizenship are as stated below next to my name.
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

AGENT FOR COLORING KERATINACEOUS FIBERS

(Title of the Invention)

the specification of which
☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY) 12/14/1999 as United States Application Number or PCT International Application Number PCT/EP99/09901 and was amended on (MM/DD/YYYY) _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached? YES	Certified Copy Attached? NO
198 59 800.9	Germany	12/23/1998	☐	☐	☒

☐ Additional foreign application numbers are listed on a supplemental priority sheet attached hereto:

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	
		☐ Additional provisional application numbers are listed on a supplemental priority sheet attached hereto.

Burden Hour Statement: This form is estimated to take .4 hours to complete. Time will vary depending upon the needs of the individual case. Any comments on the amount of time you are required to complete this form should be sent to the Chief Information Officer, Patent and Trademark Office, Washington, DC 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Assistant Commissioner for Patents, Washington DC 20231.

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I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365© of any PCT international application designating the United Sates of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(if applicable)*
	PCT/EP99/09901	12/14/1999	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☐ Firm Name OR ☐ Customer Number or label

☒ List Attorney(s) and/or agent(s) name and registration number below:

Name	Registration Number	Name	Registration Number
Wayne C. Jaeschke	21,062		
Glenn E. J. Murphy	33,539		
Stephen D. Harper	33,243		
Kimberly R. Hild	39,224		

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Please direct all correspondence to: ☒ Customer Number 00423 or label OR ☒ Fill in correspondence address below

Name	Kimberly R. Hild						
Address	Henkel Corporation						
Address	2500 Renaissance Blvd, Suite 200						
City	Gulph Mills			State	PA	Zip	19406
Country	USA	Telephone	610-278-4964	Fax	610-278-6548		

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name	**Horst**	Middle Initial		Family Name	**Hoeffkes**	Suffix e.g. Jr.	
Inventor's Signature					Date		
Residence: City	**Duesseldorf**	State		Country	**Germany**	Citizenship	**Germany**
Post Office Address	**Carlo-Schmid-Str. 113**						
Post Office Address							
City	**40595 Duesseldorf**	State		Zip		Country	**Germany**	Applicant Authority	

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

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U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number *(if applicable)*
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Name of Sole or First Inventor: ☐ A petition has been filed for this unsigned inventor

Given Name	Horst	Middle Initial		Family Name	Hoeffkes	Suffix e.g. Jr.	
Inventor's Signature	Horst Hoeffkes					Date	August 1, 2001
Residence: City	~~Duesseldorf~~ DCU	State		Country	Germany	Citizenship	Germany
Post Office Address	Carlo-Schmid-Str. 113						
Post Office Address							
City	40595 Duesseldorf	State		Zip		Country	Germany
Applicant Authority							

☒ Additional inventors are being named on supplemental sheet(s) attached hereto

(+) inside this box →

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ADDITIONAL INVENTOR(S) Supplemental Sheet

Name of Additional Joint Inventor, if any:

☐ A petition has been filed for this unsigned inventor

Given Name	Doris	Middle Initial		Family Name	Oberkobusch	Suffix e.g. Jr.	
Inventor's Signature	Doris Oberkobusch			Date	August 1, 2001		
Residence: City	Duesseldorf	State		Country	Germany	Citizenship	Germany
Post Office Address	Auf'm Rott 81						
Post Office Address							
City	40591 Duesseldorf	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any:

☐ A petition has been filed for this unsigned inventor

Given Name	David	Middle Initial		Family Name	Rose	Suffix e.g. Jr.	
Inventor's Signature				Date			
Residence: City	Hilden	State		Country	Germany	Citizenship	Great Britain
Post Office Address	Am Eichelkamp 223						
Post Office Address							
City	40723 Hilden	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any:

☐ A petition has been filed for this unsigned inventor

Given Name	Melanie	Middle Initial		Family Name	Hitz	Suffix e.g. Jr.	
Inventor's Signature	Melanie Hitz			Date	August 1, 2001		
Residence: City	Dormagen	State		Country	Germany	Citizenship	Germany
Post Office Address	Platanenstr. 10						
Post Office Address							
City	41542 Dormagen	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any:

☐ A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature				Date			
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country		Applicant Authority	

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ADDITIONAL INVENTOR(S) Supplemental Sheet

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Doris	Middle Initial		Family Name	Oberkobusch	Suffix e.g. Jr.	
Inventor's Signature						Date	
Residence: City	Duesseldorf	State		Country	Germany	Citizenship	Germany
Post Office Address	Auf'm Rott 81						
Post Office Address							
City	40591 Duesseldorf	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	David	Middle Initial		Family Name	Rose	Suffix e.g. Jr.	
Inventor's Signature	David Rose					Date	August 1, 2001
Residence: City	Hilden	State		Country	Germany	Citizenship	Great Britain
Post Office Address	Am Eichelkamp 223						
Post Office Address							
City	40723 Hilden	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name	Melanie	Middle Initial		Family Name	Hitz	Suffix e.g. Jr.	
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Residence: City	Dormagen	State		Country	Germany	Citizenship	Germany
Post Office Address	Platanenstr. 10						
Post Office Address							
City	41542 Dormagen	State		Zip		Country	Germany	Applicant Authority	

Name of Additional Joint Inventor, if any: ☐ A petition has been filed for this unsigned inventor

Given Name		Middle Initial		Family Name		Suffix e.g. Jr.	
Inventor's Signature						Date	
Residence: City		State		Country		Citizenship	
Post Office Address							
Post Office Address							
City		State		Zip		Country		Applicant Authority	

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